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MULTICOLOR ELECTROCHROMIC DOT-MATRIX DISPLAY INVESTIGATION

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The feasibility of multicolor electrochromic dot-matrix displays based on lutetium diphthalocyanine was investigated on the premise that integrated matrix drive electronics for such devices will become available in several years. A 3 x 3-inch display panel with switchable 5 x 7-dot characters was attractive and clearly legible at 24 lpi. Viewing was hardly impaired when a metal mesh overlay simulating the appearance of matrix drive circuitry was placed in registry with the dot pattern. Color resolution and memory

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Block 20. Abstract (Continued)

were demonstrated for adjacent red/green, blue/green, and red/blue areas in the matrix. Current and charge transients were recorded for constant-voltage pulses applied to areas representing 2 to 16 dots. Time constants of 10 to 20 ms were typical of the green-to-red electrochromic transition. An effective capacitance of approximately 1000 µf/cm^2 arose from the electrochemical reaction of the dye film. Also associated with that process was an area resistance, usually less than 25 ohms·cm^2. Further development of multicolor electrochromic dot-matrix displays is recommended.

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I. INTRODUCTION

Future military cockpit instrumentation systems will require versatile matrix display panels that may be viewed through wide angles in bright sunlight. The resolution must be adequate to present large amounts of alphanumeric information in page formats of the order of 6 x 6 inches. A full-color, flat-panel passive* display technology could be used to great advantage in these systems and would find many other applications. A new candidate for such purposes is an organic electrochromic technology based on the rare-earth diphthalocyanines.[1-4] This series of dye materials offers an outstanding combination of display performance characteristics. Features include multiple colors, low input voltage and energy, open-circuit memory, wide viewing angle, and legibility from low to very high ambient light intensity. Virtually a whole spectrum of colors can be generated in a single diphthalocyanine compound by varying the applied voltage. The response is fast (<50 ms to write or erase), even at a temperature as low as -50°C.

The structural formula of the diphthalocyanine is indicated in Figure 1. The metal atom connecting the two phthalocyanine dye units can be any of the fourteen lanthanide rare earths, as well as yttrium or scandium.[5] Thus, the diphthalocyanines comprise a large family of new display materials, each with its own multicolor characteristics. To construct an electrochromic display, a film of the diphthalocyanine is deposited by vacuum sublimation onto a transparent conductor such as tin oxide, in which the display pattern is defined. This dye-coated plate, initially green, is sealed into a cell containing a liquid electrolyte and a counter electrode which is located outside the viewing area. Application of d-c voltages ranging from approximately -1.5 to +1.5 V causes selected areas within the display pattern to change color. The display can be front-lighted or back-lighted. It is very attractive when projected on a large screen.

*A passive display material is one that does not emit light.

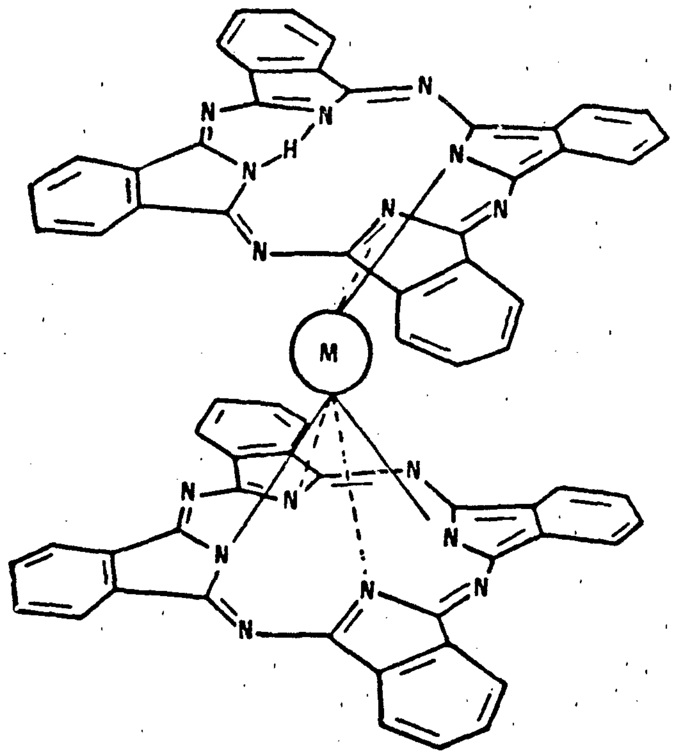


Figure 1. Molecular Structure of a Lanthanide Diphthalocyanine

(Spacing and angular placement of the rings are schematic)

The first evaluation of lutetium diphthalocyanine as an electrochromic display material was made in a Rockwell project sponsored by the Naval Air Development Center.[1,2] Performance data for this compound are summarized in Table 1. Subsequent work in these laboratories has yielded fundamental information on electrochromic mechanisms and rate-controlling processes in the diphthalocyanines.[6-8] That research is continuing under complementary Navy and Air Force programs.

The present report provides information for design of dot-matrix displays using the diphthalocyanine electrochromic technology. This study was sponsored by the Sensor and Control Technology Division of the Office of Naval Research. The experimental approach was predicated on the future availability of an electronic drive matrix that could be built into the display panel. Each dot would then be addressed through an individual switch, so that direct multiplexing to the display material would be unnecessary. Thin-film-transistor technology[9,10] may offer the best approach for the active-matrix drive.

The project had several objectives: To show the appearance of a 3 x 3-inch, 24 lines-per-inch (lpi) matrix panel using lutetium diphthalocyanine as the multicolor material; to determine the electrical switching characteristics of individual dots or small groups of dots in such a panel; and to demonstrate resolution and memory for dots surrounded by areas of a different color. The results include photographs and equivalent-circuit parameters that help to define the drive requirements. We conclude that further experimental development of multicolor electrochromic dot-matrix displays is fully merited.

TABLE 1

SUMMARY OF DISPLAY CHARACTERISTICS FOR LUTETIUM DIPHTHALOCYANINE

Multiple colors	Red, green, blue, violet, and others; high chroma on Munsell scale.(1)
Unrestricted viewing	Wide angle; low light levels to sunlight; appearance enhanced in bright light; can be back-lighted or projected on screen.
Low input voltage	1.5 to -1.5 V d-c
Low switching energy	~2 mJ/cm^2
Nonvolatile memory	Minutes to hours on open circuit.
Fast response	<50 ms (See Section III for detail.)
Wide operating temperature range	-50° to 100°C without visible change in switching speed*.
Cycle life	$5x10^4$ red/green or red/blue in early tests.

*-50°C in 30 wt% $CaCl_2$ electrolyte.

II. EXPERIMENTAL PROCEDURES

This section describes the materials, display designs, fabrication processes, and evaluation methods that were used in the dot-matrix study.

A. MATERIALS

Lutetium diphthalocyanine was prepared from lutetium acetate and o-phthalonitrile, as described in a previous report.[1] The tin oxide-glass plates were 4 x 4-inch pieces from Corning Glass Works, fabricated by a chemical spraying process. Sheet resistivities were in the range of 8 to 10 or 21 to 24 ohms/square. The electrolyte was 1 M aqueous potassium chloride, air-free in the sealed cells, and air-saturated in the open cells that were used for the green-to-red transient measurements. The counter and reference electrodes were silver-silver chloride (Ag/AgCl) prepared by coating silver foil with porous silver and anodizing it in the 1 M KCl electrolyte. This counter electrode system was chosen for experimental convenience. A less expensive electrode containing no silver could be developed for use in practical displays.

B. DISPLAY DESIGNS AND FABRICATION

Without matrix drive circuitry, every dot in the test panels could not be independently addressed. Hence, the experimental displays were designed to have the appearance of a 3 x 3-inch dot matrix but to offer limited pattern selection. Only certain groups of dots forming letters, numbers, or stripes could be written and erased, while the surrounding field of background dots remained green. This was accomplished in the following way: Switchable dye dots were in contact with the conductive tin oxide, while unswitchable dots in the background area were insulated from the tin oxide by a layer of silicon dioxide. Etch lines in the tin oxide film isolated the switchable characters from one another.

Three types of display plates were constructed as indicated in Table 2. Design details are given in Table 3, and prints made from the photomasks are shown in Figures 2 through 4. In the transient test plate, the switchable areas were surrounded by insulated tin oxide. The resolution/memory panel was designed to show a few switchable dots almost surrounded by larger switchable backgrounds. (Due to a fabrication error, a different pattern with large adjacent switchable areas was actually obtained.)

The plates were fabricated by photolithographic methods, using Shipley 1350J positive photoresist. Iron oxide masks for the tin oxide, insulator, and dye layers were produced with a computer-aided design technique. The principal steps in fabrication of a 3 x 3-inch display plate were as follows:

(1) Lines were etched in the tin oxide with zinc dust and a solution composed of dilute sulfuric acid and methanol, after appropriate photodelineation of a spun-on layer of photoresist.

(2) The insulator film was deposited by a chemical vapor deposition silox process. This process involves the gaseous reaction of silane gas with oxygen at an elevated temperature to form a continuous pinhole-free coating of SiO_2 on the display plate surface.

(3) The insulator was etched in the desired pattern with a buffered fluoride (bifluoride plus hydrofluoric acid) etch solution after a second photodelineation with the appropriate photomask.

(4) A copper in-contact mask for the dye pattern was fabricated on top of the insulator-tin oxide plate by vacuum deposition and photodelineation.

TABLE 2

DESIGNS OF EXPERIMENTAL DISPLAY PLATES*

Plate	Purpose	Description	Mask Designs
1	Demonstrate the appearance of a 24-lpi multicolor dot matrix display with 5x7-dot characters.	3x3-inch matrix with switchable numbers, letters, and lines.	Figure 2
2	Determine electrical switching transients.	4 switchable areas of 1 to 16 dots surrounded by insulated tin oxide.	Figure 3
3	Demonstrate resolution and memory.	6 switchable areas of 1 or 2 dots almost surrounded by larger switchable background.	Figure 4

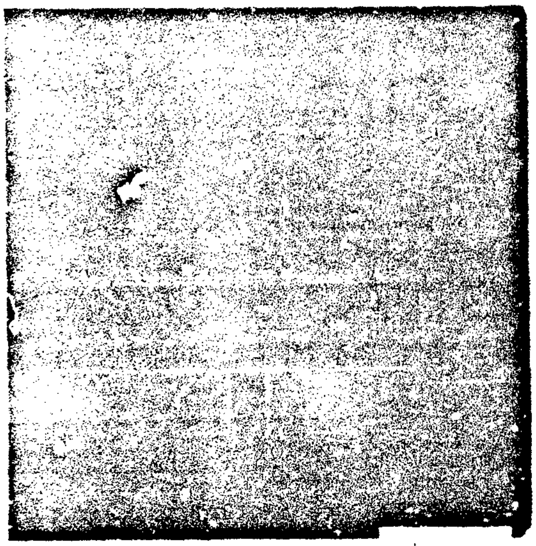
*Dimensions are given in Table 3.

TABLE 3

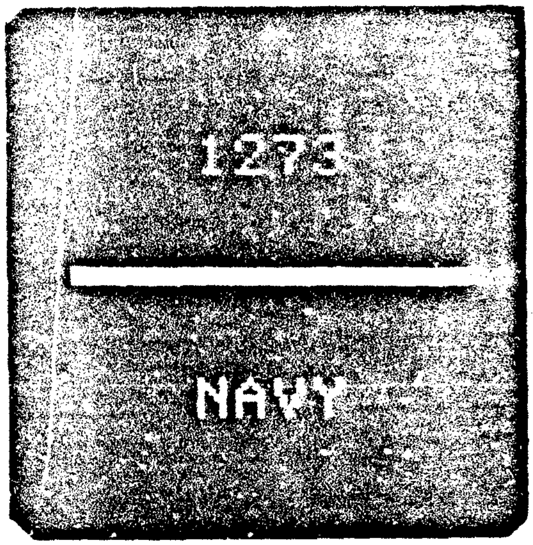
DIMENSIONS IN EXPERIMENTAL DISPLAYS

Matrix Dimensions	
Side of square dye dot	931 µm
Dot repetition distance	1058 µm
Dot separation	127 µm
Etch lines in tin oxide	51 µm
Plate No. 1	
Viewing area	7.62x7.62 cm (3x3 in.)
Total dots in viewing area	5184
Alphanumeric characters	5x7 dots
Spacing between characters	2 dots
Cell thickness	0.95 cm
Drive Matrix Simulator (Overlay)	
Line width	127 µm
Line repetition distance	1058 µm
Plate No. 2	
Switchable areas	1, 2, 4, 16 dots
Insulated tin oxide fields	1.7x1.7 cm
Width of silver coated tin oxide strip	0.35 cm
Plate No. 3	
Viewing area	4.4x4.4 cm
Switchable areas*	1 or 2 dots
Surrounding switchable fields (excluding green strip)*	7x7 dots
Cell thickness	0.95 cm

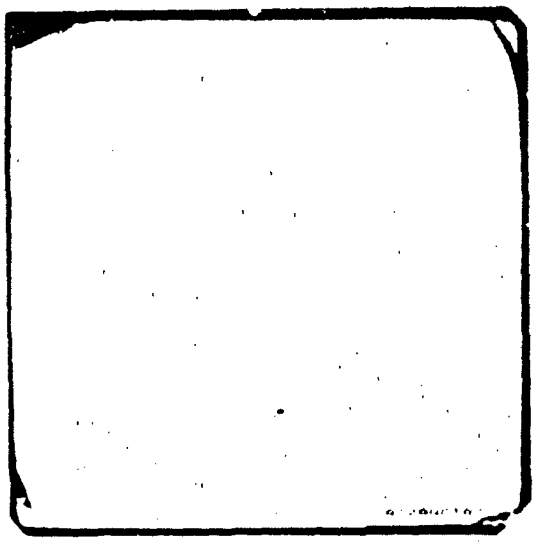
*Switchable areas differed from design, due to a fabrication error.



(a) Conductor Mask

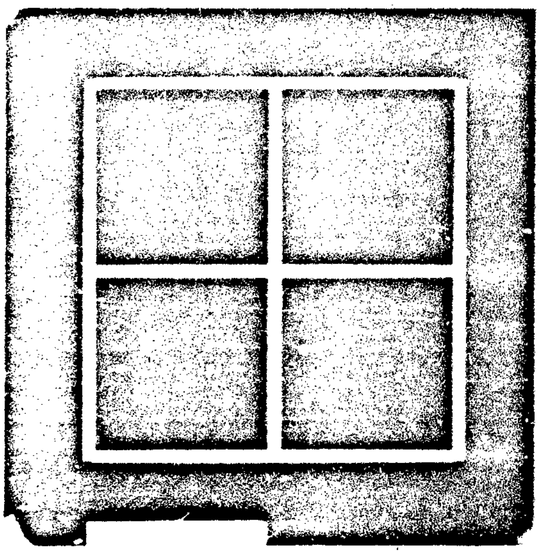


(b) Insulator Mask

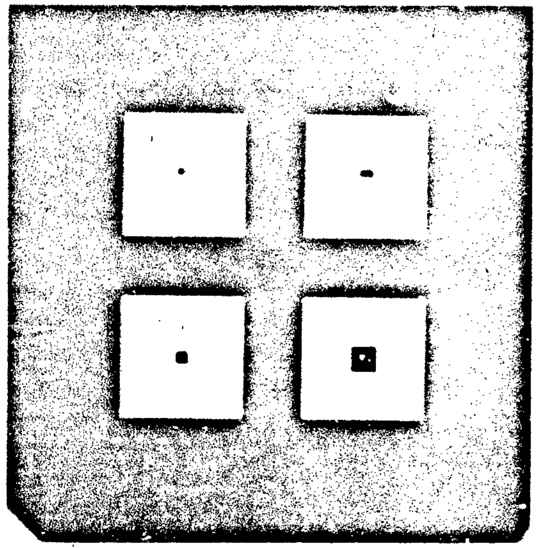


(c) Dye Mask

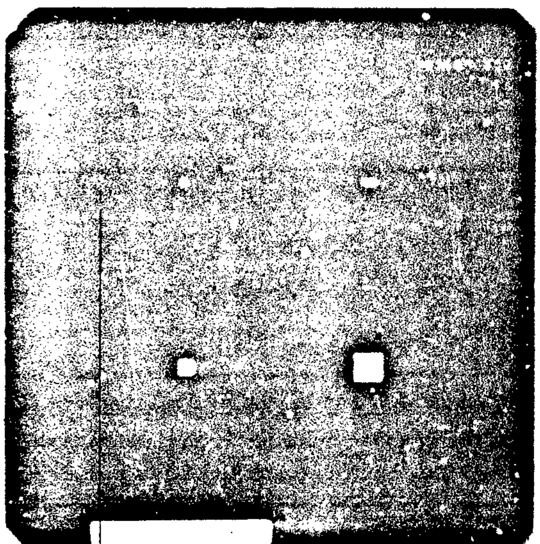
Figure 2. Masks for 3 x 3-Inch Display



(a) Conductor Mask

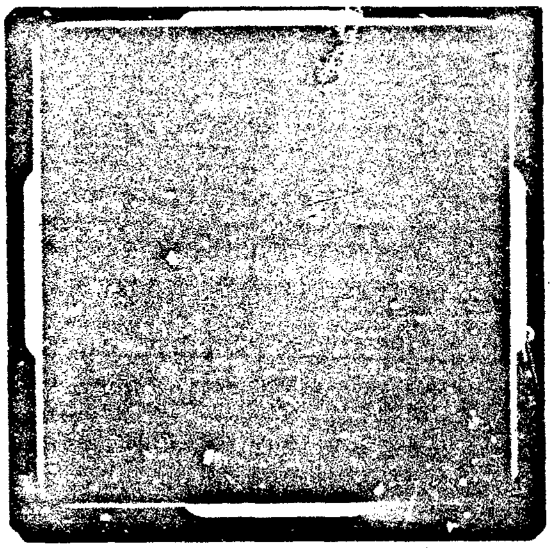


(b) Insulator Mask

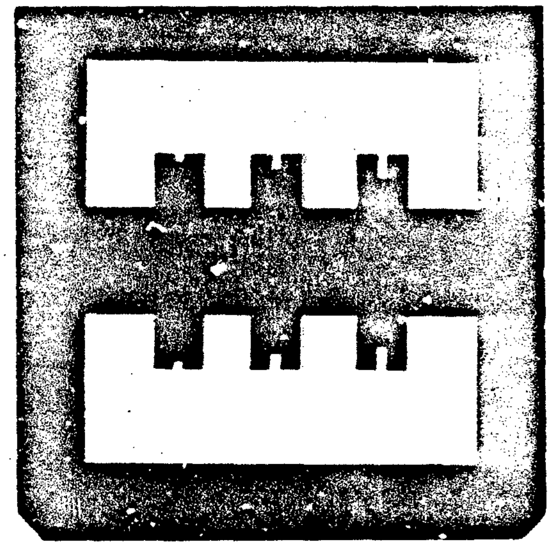


(c) Dye Mask

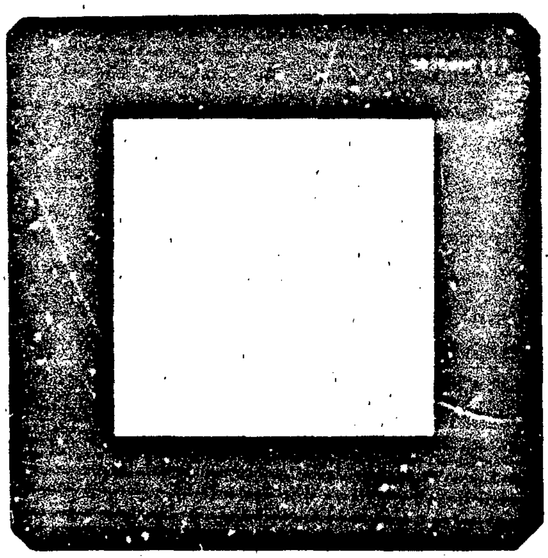
Figure 3. Masks for Transient Test Plate



(a) Conductor Mask



(b) Insulator Mask



(c) Dye Mask

Figure 4. Masks for Resolution/Memory Test Panel

(5) The dye was vacuum-sublimed over the copper mask.

(6) The copper mask and the dye on top of it were removed with a cupric chloride plus ammonia etchant. This left a matrix of separate dye dots over the entire panel area.

The matrix plates were attached to Lucite housings with a flexible silicone sealant, Dow Corning RTV Type 3140, which cures at room temperature in moist air. The cell structure for a 3 x 3-inch panel is illustrated in Figure 5. Electrical connections to the switchable characters and lines were made through silver paste contacts applied on the edges of the plate, which extended outside the cell housing.

C. EVALUATION METHODS

The sealed display panels were back-lighted through translucent glass plates. These displays were activated with a portable potentiostatic drive unit to show patterns in red or blue, which were photographed with Polaroid Type 58 Polacolor 2 film. Electronic flash lighting gave the best results for the red characters, while daylight photofloods were preferred for the blue. For this report, the color originals of the 3 x 3-inch panel were rephotographed in black and white, using a red filter to enhance the contrast. The resolution/memory panel was photographed directly in black and white, as well as color.

For determination of transient responses, test areas of dye equivalent to 2, 4, and 16 dots were activated with voltage pulses from a Princeton Applied Research (PAR) Model 173 potentiostat controlled by a Model 175 universal programmer. Figure 6 shows a photograph of the test assembly. The resulting current and charge transients were recorded on a Tektronix 564B dual-trace storage oscilloscope. Known resistances were then added in series with the cell to demonstate effects that could occur with resistive drive circuitry. The functional dependence of the transients on added resistance also permitted evaluation of circuit parameters for the electrochromic switching process.

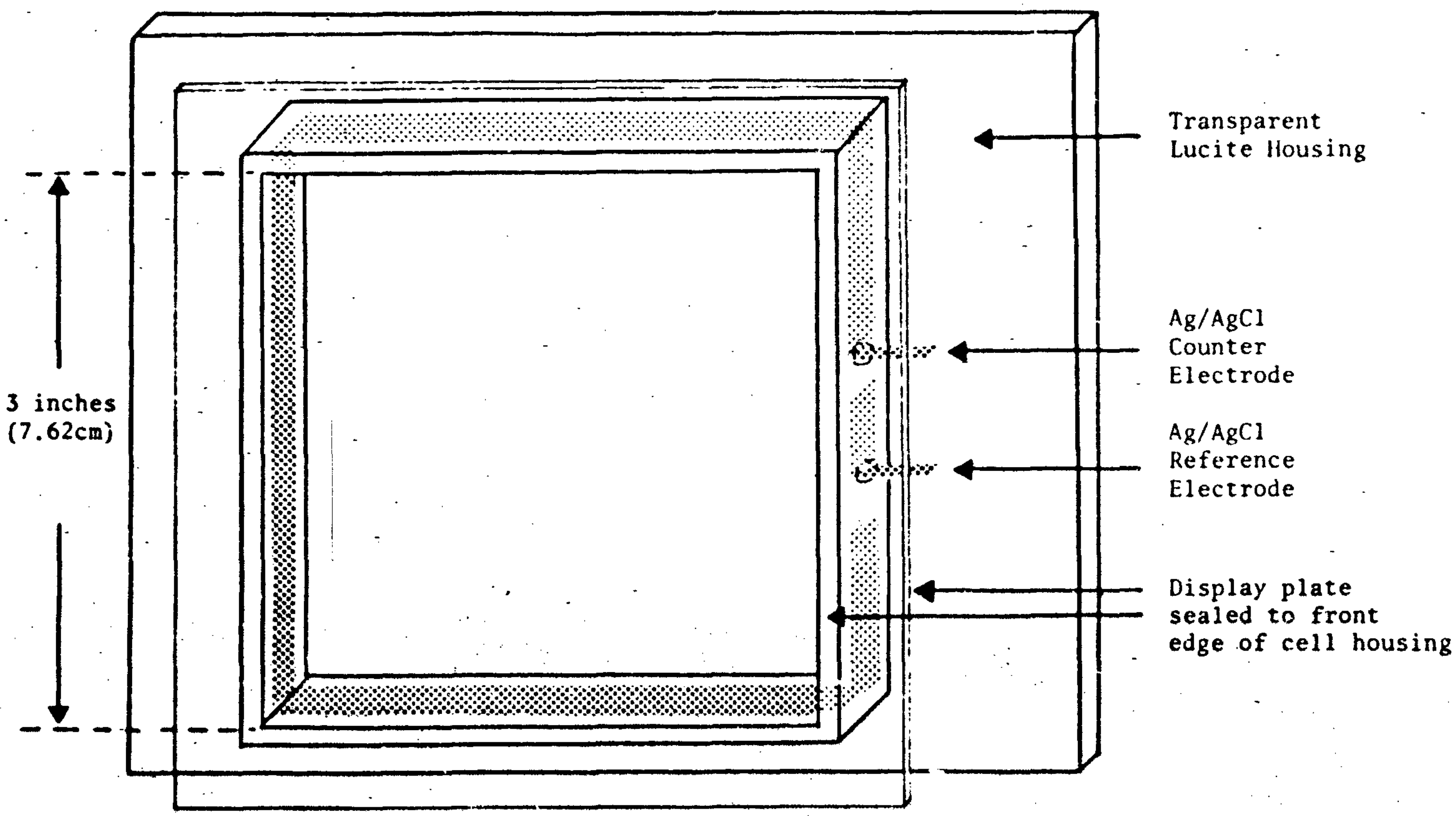


Figure 5. Structure of Electrochromic Display Cell

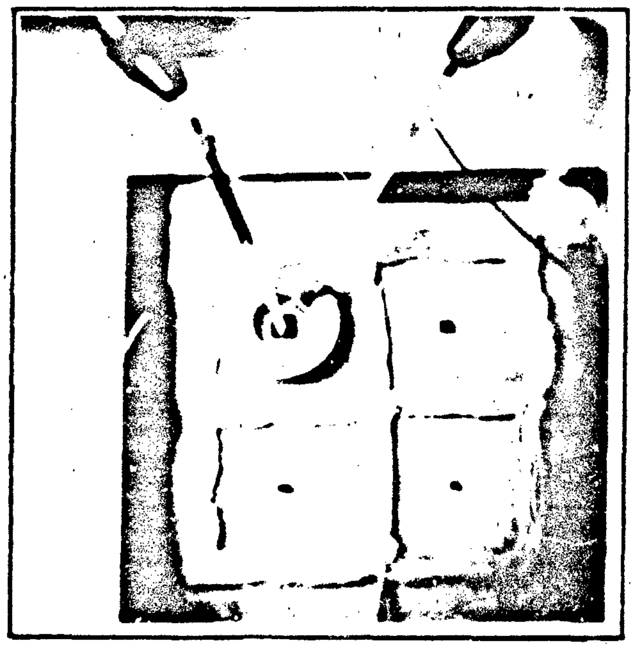


Figure 6. Test Assembly for Transient Measurements

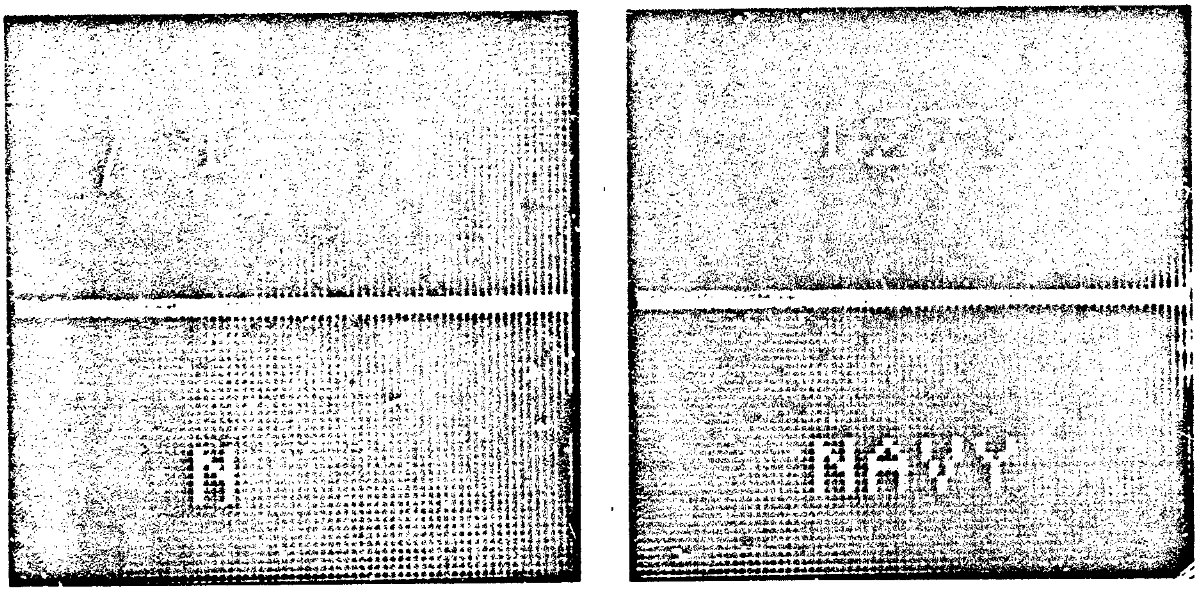
III. RESULTS AND DISCUSSION

The appearance of a 3 x 3-inch dot matrix panel is described and documented photographically in Part A of this section. Results of the transient study are presented in Part B, and the demonstration of resolution and memory at 24 lpi is reported in Part C.

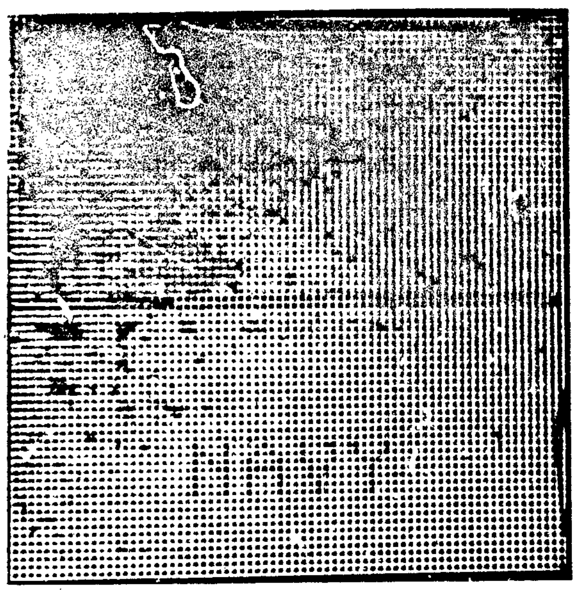
A. 3 x 3-INCH MATRIX PANEL

Black-and-white photographs of a back-lighted 3 x 3-inch matrix panel in different written stages are reproduced in Figure 7. A copper screen overlay on a separate piece of glass was attached to the outside of the cell to simulate the appearance of integrated matrix drive circuitry. The 127-μm lines of this screen were spaced to coincide with the open areas between the dye dots. With perfect registry of the patterns, there would have been no leakage of light around the dots. A splotched appearance actually resulted, due to parallax between the copper screen and the plane of the electrochromic material, which allowed some light to pass through. This is an artifact of the simple overlay arrangement; it would not occur with a drive matrix actually built into the display plate. In areas where good pattern registry occurred, it was apparent that the drive matrix would not be visually objectionable at 24 lpi, although the opaque "drive" structure occupied 23 percent of the viewing area. A drive matrix of the same lire width probably would be acceptable even at 50 lpi. For higher resolution, the microelectronic structure should be scaled down in proportion to the dot size.

Figure 7 shows that switching occurred with good pattern definition, but these black and white images cannot portray the aesthetic quality of the display. The red and blue characters on the green background were attractive and clearly legible. A set of the original color photographs was provided under separate cover to the Office on Naval Research.



(a) Red Characters on Green Background



(b) Blue Characters on Green Background

Figure 7. Photographs of 3 x 3-Inch Display

B. ELECTRICAL TRANSIENTS

The electrochromic film can be switched by application of a constant current, a constant voltage, or a time-dependent input signal. Although constant-current input provides responses amenable to simpler theoretical interpretation,[6,7] this method is not recommended for a display cell because the dye electrode may be inadvertently driven to higher voltages at which the electrolyte is decomposed. With three-electrode potentiostatic control, which was used in this study, the overdriving problem can be avoided, and the measured response is that due to the dye electrode plus any resistance deliberately connected in series with it. The three electrodes are the display electrode, the reference, and the counter electrode. Once a practical counter electrode is fully developed, it can serve as a reference electrode as well. A simpler two-electrode drive can then be used. Details of the potentiostatic method for driving experimental cells are given in a previous report.[1]

Electrical parameters sought in the present work included time constants, peak currents, and switching charges. A description of the transient behavior of the display electrode, or matrix dot, in terms of an equivalent circuit containing resistive and capacitive elements was also desired. The transient analysis is developed on an operational basis in Parts 1-3 below. The physical significance of the resulting circuit parameters in relation to the electrochromic reaction mechanism is then discussed in Part 4.

1. Transient Shapes, Time Constants, and Initial Currents

The potentiostatic program for switching the dye from green to red and back to green was as follows:

E_1 0.00 ± 0.05 V vs Ag/AgCl
Adjusted manually for zero current through the dye electrode.

E_2 1.50 V or 2.00 V

Switching pulse of 100 to 500 ms, depending on dye area and amount of series resistance; color changed from green to red.

E_3 Small negative pulse of about the same length to switch back to green.

E_4 0.01 V

Final level, essentially the open-circuit condition for green; remained here until charge returned to zero.

Typical current and charge transients obtained with this switching routine are shown in Figure 8. Qualitatively, the curves resembled those of a resistor and capacitor in series. However, instead of approaching zero asymptotically, as the current in that system would do, the display current reversed direction toward the end of the charging pulse and continued at a low level in opposition to the driving voltage. Correspondingly, the accumulated charge passed through a maximum value q_{lim} as the current reversed; it then slowly diminished.

For a simple resistor R and capacitor C in series, the current i should decay exponentially in accordance with Equation (1).

$$i = [(E_2 - E_1)/R] \exp(-t/RC) \quad (1)$$

Although the electrochromic system is more complicated, it was of interest to examine the plot of log i vs t suggested by this equation. Figure 9 shows a series of these plots for a 16-dot dye area with added resistance R_a ranging from 0 to 600 ohms. Similar sets of straight lines were obtained for the 4-dot and 2-dot areas. A time constant τ could be evaluated from the slope:

$$\tau = RC = -1/(d\ell n\ i/dt) \quad (2)$$

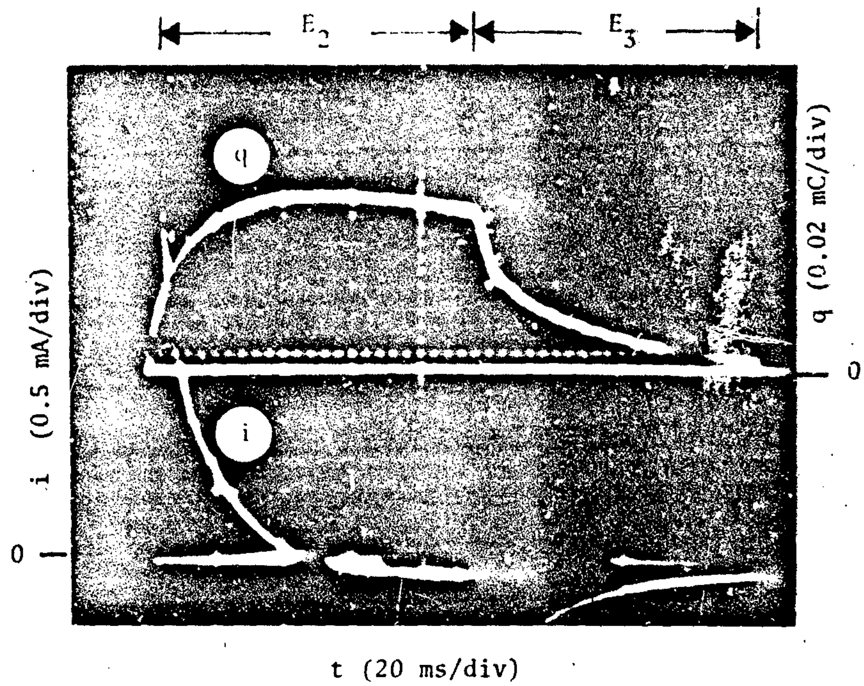


Figure 8. Current and Charge Transients on 2-Dot Area for 2.0-V Pulse Without Added Resistance

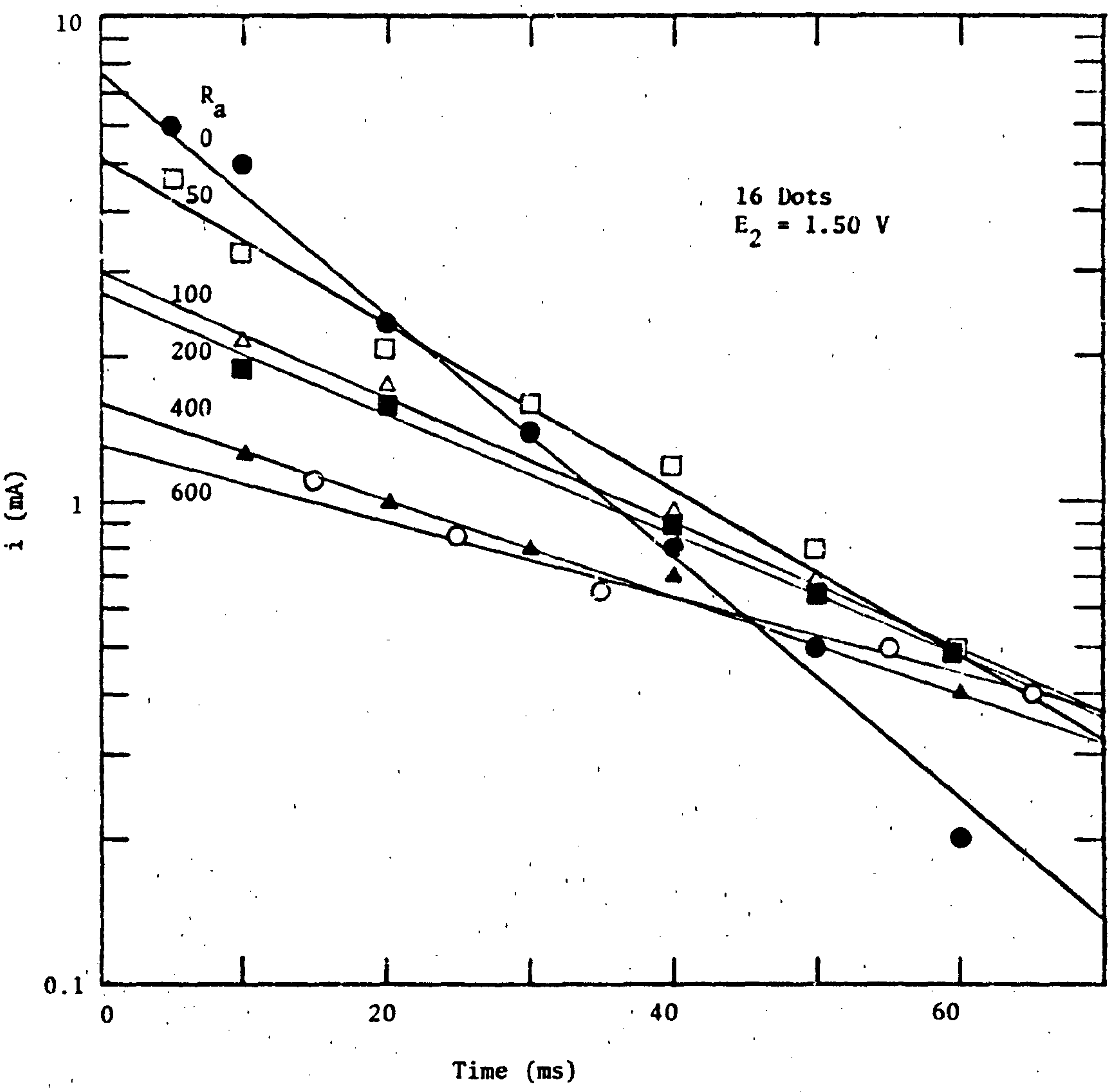


Figure 9. Evaluation of $i_{t=0}$ and τ for Different Values of R_a

A current parameter $i_{t=o}$ was also found by extrapolating the linear plot to zero time. The actual peak current at the beginning of the pulse could not be determined accurately because the oscilloscope trace was initially very steep. Moreover, the extrapolated current represents the system with an infinitesimal number of red molecules present in addition to the green. This concept is useful in a chemical model.

Transient data, including the time constants and extrapolated initial currents, are given in Table 4. The values of τ are consistent with switching times well below 50 ms that are generally observed for lutetium diphthalocyanine. Without added resistance, only the 4-dot area had a time constant greater than 50 ms. This might have been due to nonuniformity or surface contamination of the dye film or the tin oxide substrate.

2. Resistance Parameters

The total resistance R_t of the display electrode circuit can be expressed as the sum of three terms

$$R_t = R_o + R_c + R_a \tag{3}$$

where R_o represents an effective resistance within the dye film and its interfacial regions under current flow; R_c is the resistance of the transparent conductor; and R_a is the added series resistance. With the reference electrode located near the dye surface, the electrolyte resistance could be neglected.

The tin oxide resistance R_c was also negligible, even with the smallest dye areas used in these experiments. This was shown by the approximation method outlined in Figure 10. The concentric-circle model is closely related to the test-plate geometry and is mathematically much simpler. Calculated resistances for several values of r_o/r_i are given in Table 5. These estimates indicate that R_c was below 5 ohms in the transient test plates. The last two rows of the table show that a large

TABLE 4

TRANSIENT DATA FOR SWITCHING ELECTROCHROMIC FILM UNDER CONSTANT-VOLTAGE PULSES[a]

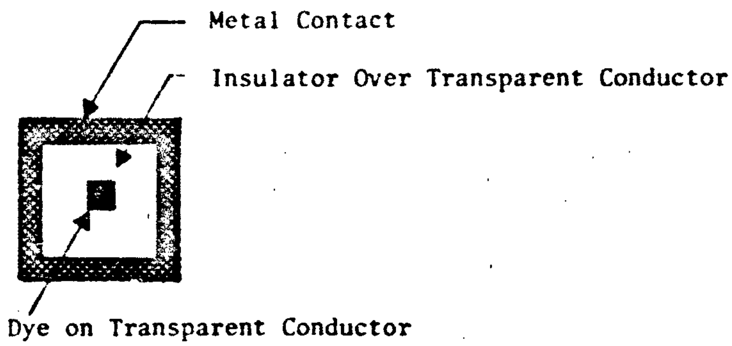
Dye Area (Dots)[b]	E_2 (V)	R_a (ohms)	$i_{t=o}$ (mA)	q_{lim} (mC)	τ (ms)	R_o (ohms)	E' (V)
2	1.50	0	1.38	0.030	18	1350	-0.38
		100	1.18	0.029	22		
		500	0.90	0.024	27		
		1000	0.68	0.021	28		
		4000	0.45	0.017	34		
		8000	0.195	0.011	50		
2	2.00	0	3.55	0.052	11	440	0.30
		500	2.10	0.036	17		
		1000	1.08	0.032	30		
		4000	0.40	0.019	50		

[a]Initial optical density at 670 nm was 1.30.

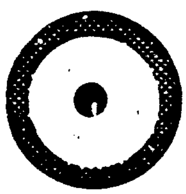
[b]1 dot = 8.5×10^{-3} cm^2.

TABLE 4 (CONTINUED)

Dye Area (Dots)	E_2 (V)	R_a (ohms)	$i_{t=o}$ (mA)	q_{lim} (mC)	τ (ms)	R_o (ohms)	E' (V)
4	1.50	0	0.90	0.075	65	1420	0.18
		400	0.72	0.056	69		
		2000	0.36	0.034	82		
		4000	0.24	0.022	83		
16	1.50	0	7.7	0.165	18	117	0.61
		50	5.2	0.150	26		
		100	3.0	0.135	33		
		200	2.8	0.115	34		
		400	1.6	0.090	44		
		600	1.3	0.075	56		



(a) Transient Test Pattern for 16-Dot Dye Area



$$R_c = \frac{\rho_s}{2\pi} \int_{r_i}^{r_o} \frac{dr}{r} = \frac{\rho_s}{2\pi} \cdot ln \frac{r_o}{r_i}$$

R_c	Resistance of transparent conductor from metal contact to dye dot
ρ_s	Sheet resistivity of transparent conductor
r_o	Outer radius of transparent conductor (inner radius of metal contact)
r_i	Inner radius of transparent conductor (radius of dye dot)

(b) Circular Model

Figure 10. Method for Estimation of Tin Oxide Resistance in Transient Test Plate

TABLE 5

ESTIMATED RESISTANCE OF TRANSPARENT CONDUCTOR
IN TRANSIENT TEST PLATES[a]

Test Pattern	Corresponding r_o/r_i	Approximate R_c/ρ_s (squares)	Approximate R_c (ohms)[b]
16 Dots	4.6	0.24	2.4
2 Dots	9.2	0.35	3.5
1 Dot	18.4	0.46	4.6
--	535	1.00	10
--	2.9×10^5	2.00	20

[a]Based on concentric-circle approximation (Figure 10).

[b]Taking ρ_s = 10 ohms/square.

matrix drive plate through which any dot might be addressed with a suitable switching array would not, in itself, contribute significant resistance unless the sheet resistivity ρ_s were very large or the resolution of the matrix were unrealistically high.

The total resistance R_t can now be expressed as

$$R_t = R_o + R_a \tag{4}$$

Equation (1) suggests that R_t might be evaluated from $i_{t=o}$. This is not feasible, however, in the case of the electrochromic system because only part of the applied voltage is effective in driving the electrochemical reaction. One cannot simply take $R_t = (E_2 - E_1)/i_{t=o}$, but should at least include a term E' representing a back emf of the electrochemical process. As an approximation, then

$$R_o + R_a = (E_2 - E_1 - E')/i_{t=o} \tag{5}$$

It is recognized that Equation (5) may be oversimplified; the nature of the dye electrode process[6,7] suggests that R_o and E' may not be constant. It is of interest, nevertheless, to examine the data with respect to this equation.

Since E_1 happened to be near zero* in all of the experiments, Equation (5) can be rewritten in the form

$$1/i_{t=o} = [1/(E_2 - E')]\,(R_o + R_a) \tag{6}$$

If conditions were such that both E' and R_o could be treated as constants, a plot of $1/i_{t=o}$ vs R_a would be linear. The resistance R_o would be found from a negative intercept on the R_a axis, and E' would be determined from the slope.

*This is a fortuitous result of using an Ag/AgCl reference electrode.

Plots of this kind for the experimental transients are shown in Figures 11-14. Nearly all of the points did fall on straight lines, and a negative resistance intercept was obtained in every case. The values of R_o and E' found in this way are included in Table 4.

3. Capacitance Parameters

For a simple series resistance-capacitance model, the value of C could be determined easily from dependence of the time constant on total resistance. Thus, a plot of τ vs R_a would have a slope equal to C and an intercept on the time axis equal to R_oC. In Figure 15, the values of τ from the logarithmic current plots are shown as functions of the resistance-area product R_aA. This plotting variable was used instead of resistance so that the curves for all of the dye areas could be presented on the same graph.

Although only one of these plots was linear, three of them had rather consistent intercepts in the range of 10 to 20 ms. It was noted previously that the 4-dot area switched more slowly, due apparently to some extraneous resistance. The one linear plot of τ vs R_aA, for the 2-dot area with a 2.0-V pulse, had a slope corresponding to a capacitance of 570 $\mu f/cm^2$, or 4.8 μf/dot. It should be noted that this capacitance was evaluated for conditions involving large amounts of series resistance. It is considerably smaller than 1480 $\mu f/dm^2$, or 12.6 μf/dot, which was determined for the same pulse height at zero added resistance by means of Equation (7).

$$C_o/A = \tau_o/(\kappa_o A) \tag{7}$$

4. Circuit Parameters and the Electrochromic Mechanism

Our previous research has shown that the green-to-red transformation of lutetium diphthalocyanine [$LuH(Pc)_2$] in a chloride electrolyte proceeds through the reaction

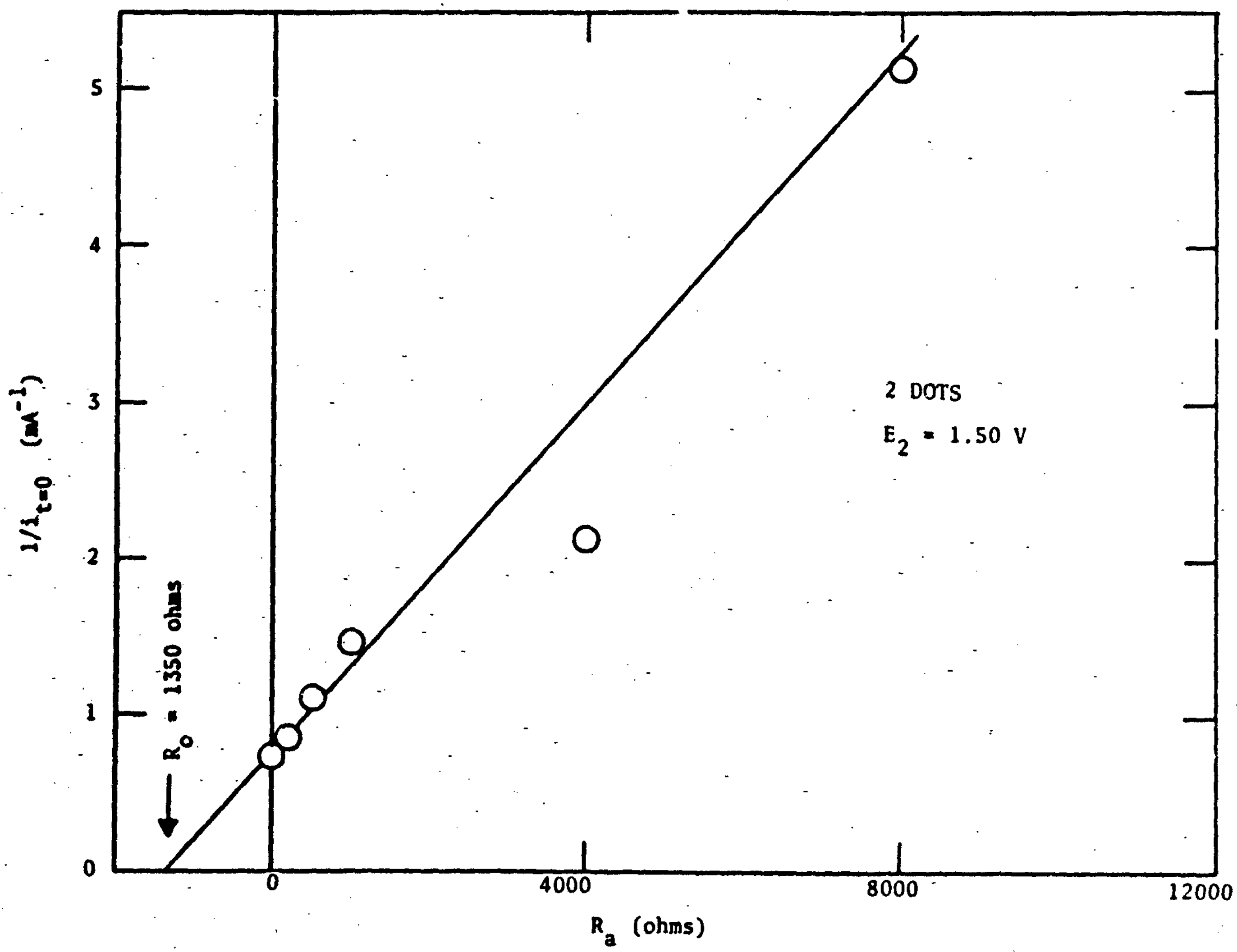


Figure 11. Dependence of $i_{t=0}$ on R_a for 2-Dot Area with 1.5-V Pulse

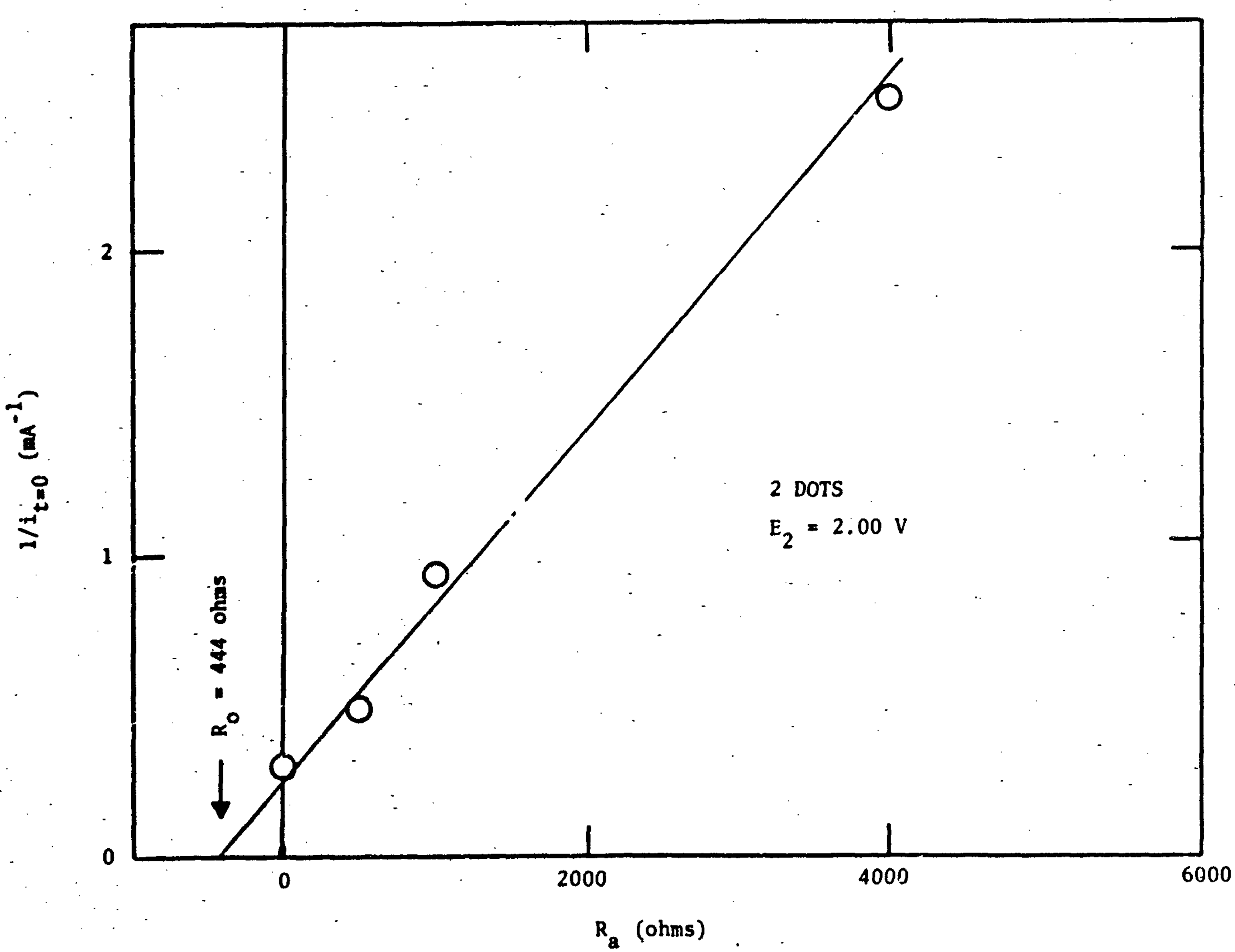


Figure 12. Dependence of $i_{t=0}$ on R_a for 2-Dot Area with 2.0-V Pulse

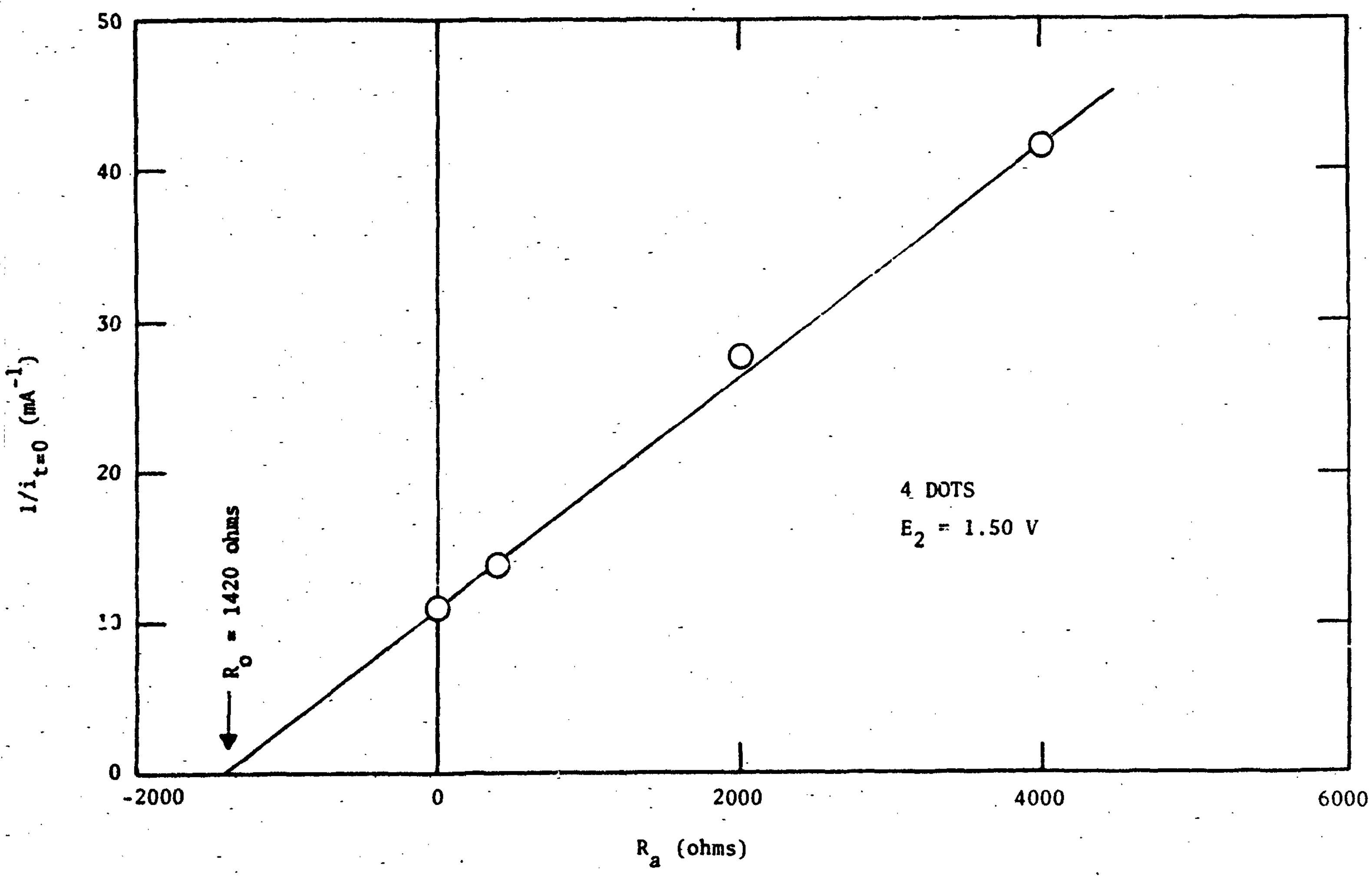


Figure 13. Dependence of $i_{t=0}$ on R_a for 4-Dot Area with 1.5-V Pulse

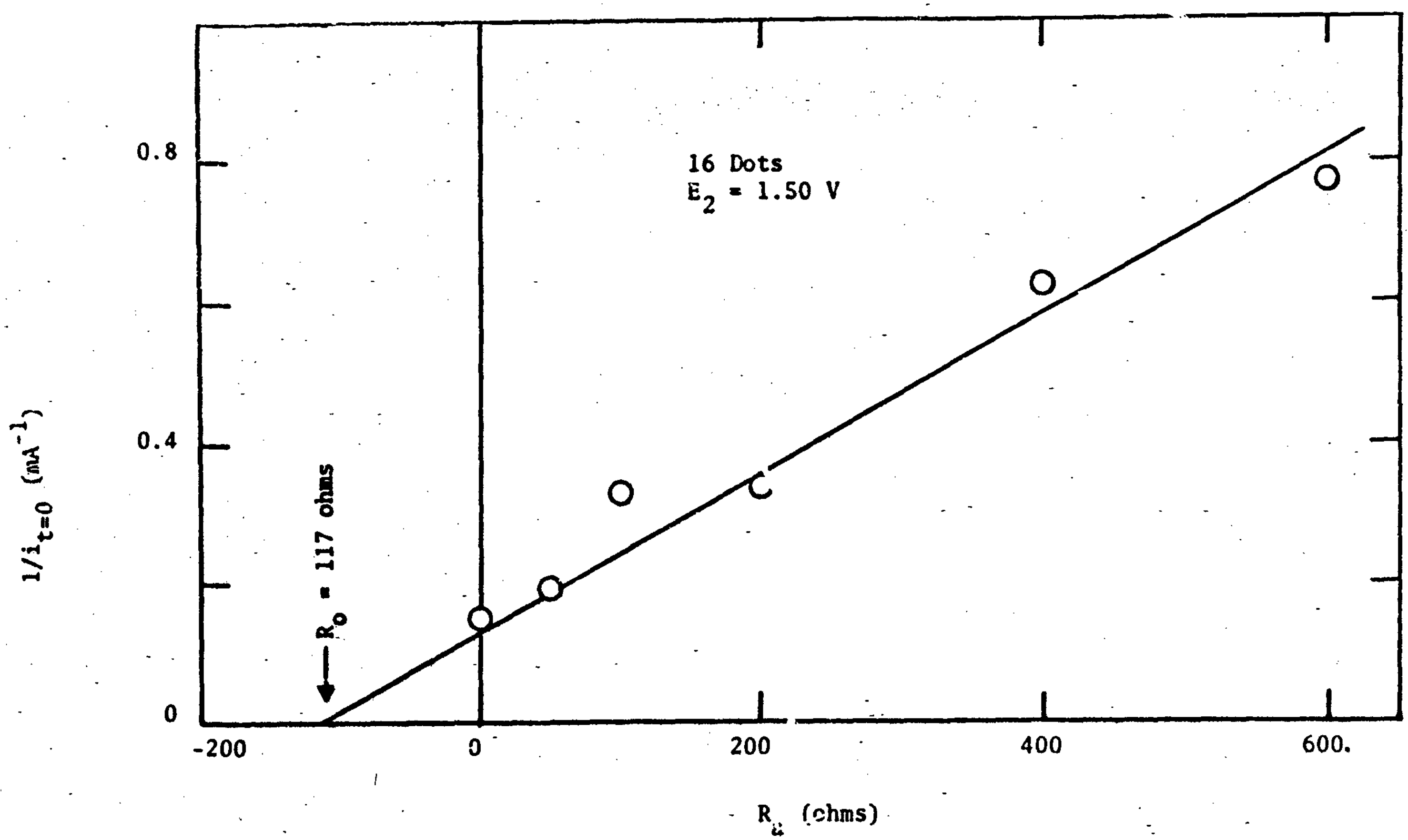


Figure 14. Dependence of $i_{t=0}$ on R_a for 16-Dot Area with 1.5-V Pulse

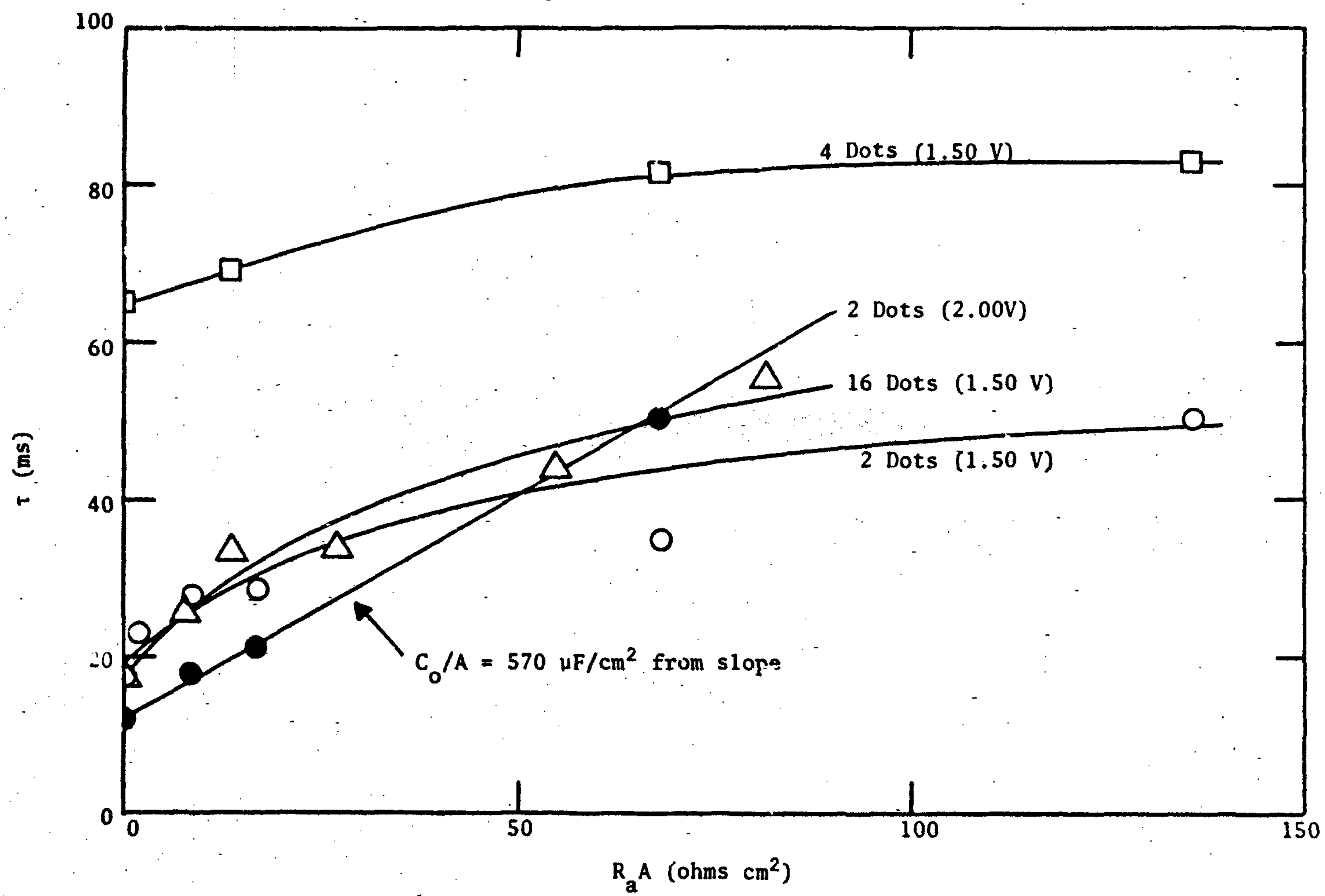


Figure 15. Dependence of Time Constant on Added Resistance

$$LuH(Pc)_2 + nCl \rightarrow LuH(Pc)_2{\cdot}nCl + ne$$

Green Red

The number of electrons n appeared to be two for the elemental process, but significant deviations from n = 2 have been observed.[6-8] This electrochemical reaction accounts for the very large capacitance associated with the switching process. Since the electrons removed from the dye are compensated by anions, the appropriate equivalent circuit element is a pseudocapacitor rather than a conventional parallel-plate condenser.

A galvanostatic transient study led to a p... ical description of the switching mechanism.[7] Those results indicated that the red/green boundary traveled through the film from the solution interface toward the tin oxide surface. The rate-controlling factor was a space change in the red film. Clearly, a constant resistance in series with the pseudocapacitance cannot adequately represent such a system. However, the RC model still provides a useful frame of reference. It predicts, for example, that the time constant τ_o of the display electrode should be independent of the dye area, since the capacitance C_o should be directly proportional to the area, while the resistance R_o should be inversely proportional to area.

The electrical parameters for a unit area of dye in the absence of added resistance are given in Table 6. The time constant τ_o was essentially the same for the 2-dot and 16-dot test areas, although R_oA and C_o/A depended on the pulse height.

It is of interest to compare the experimental charge density q_{lim}/A with that predicted from the electrochemical reaction. For the dye thickness used in the transient measurements, a value of 3.02 mC/cm^2 would correspond to n = 2. Only at the higher pulse of 2.0 V, with $R_a = 0$, was this charge density actually attained. The added series resistance was expected to delay the switching process. It is now apparent that it

TABLE 6

ELECTRICAL PARAMETERS FOR UNIT AREA OF DYE FILM WITHOUT ADDED RESISTANCE[a]

Dye Area (Dots)	E_2 (V)	τ_o (ms)	$i_{t=o}/A$ (mA/cm^2)	q_{lim}/A[b] (mC/cm^2)	R_oA ($ohms \cdot cm^2$)	C_o/A[c] ($\mu f/cm^2$)
2	1.50	18	81	1.8	23	780
2	2.00	11	209	3.1	7.5	1480
4	1.50	65	26	2.2	48	1340
16	1.50	18	57	1.2	16	1100

[a]Initial optical density at 670 nm was 1.30.

[b]Limiting charge density for $n = 2$ would have been 3.02 mC/cm^2.

[c]Apparent capacitance $C_o/A = \tau_o/(R_oA)$.

also affected the extent of completion of the electrochromic reaction. This is shown directly in Table 4, and indirectly in Figure 16, where q_{lim}/A is plotted against the extrapolated initial current density $i_{t=o}/A$. The extrapolated current bears an inverse relationship to the total resistance R_t in the dye electrode circuit. It will be recalled that q_{lim} was evaluated at the point of current reversal. This interesting feature of the transients has not yet been explained on a mechanistic basis. It will be investigated in our continuing basic research program. Meanwhile, it is significant that the electrochromic display may be switched more completely when it is switched rapidly. From a display-engineering viewpoint, this is a favorable situation.

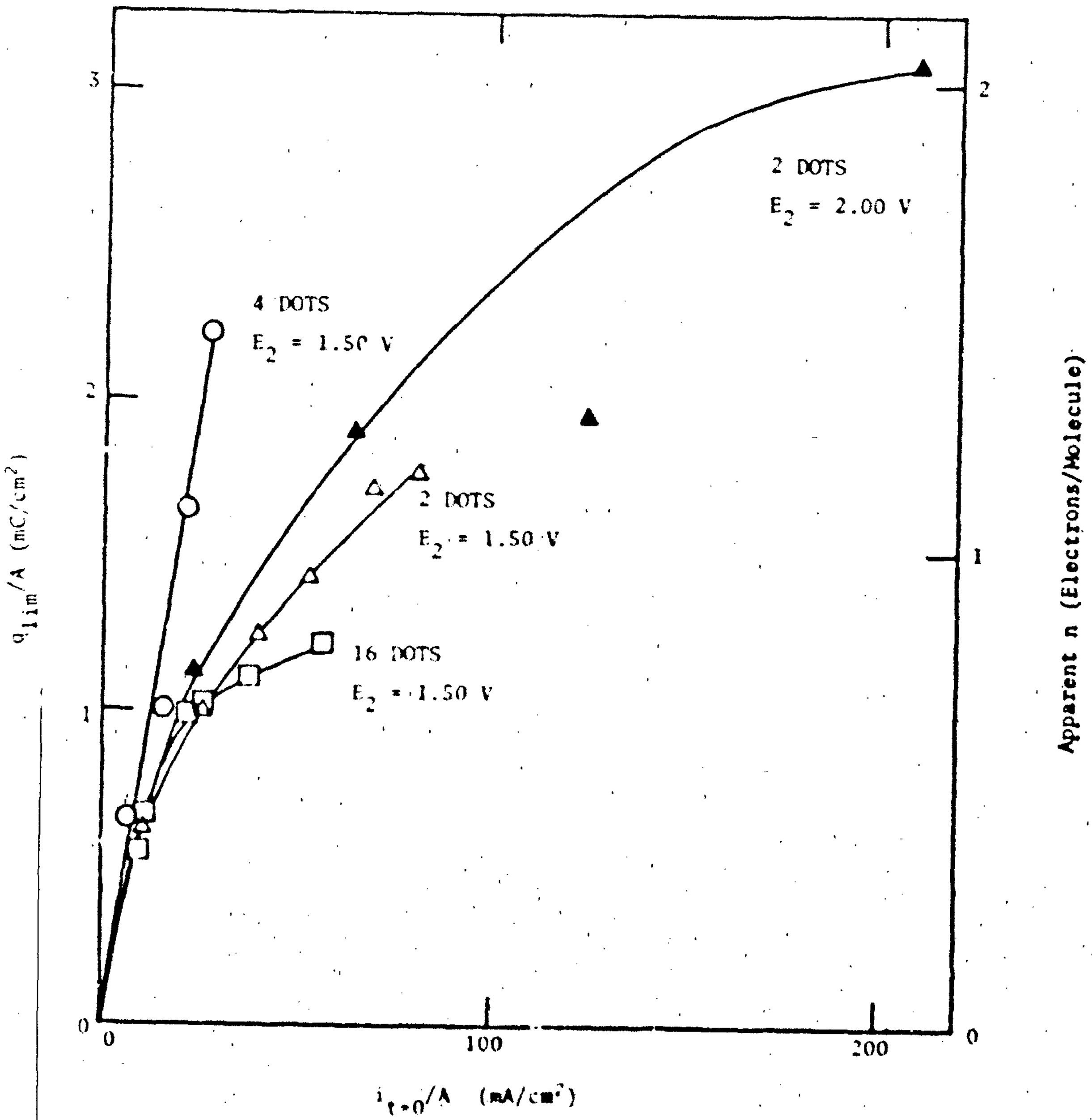


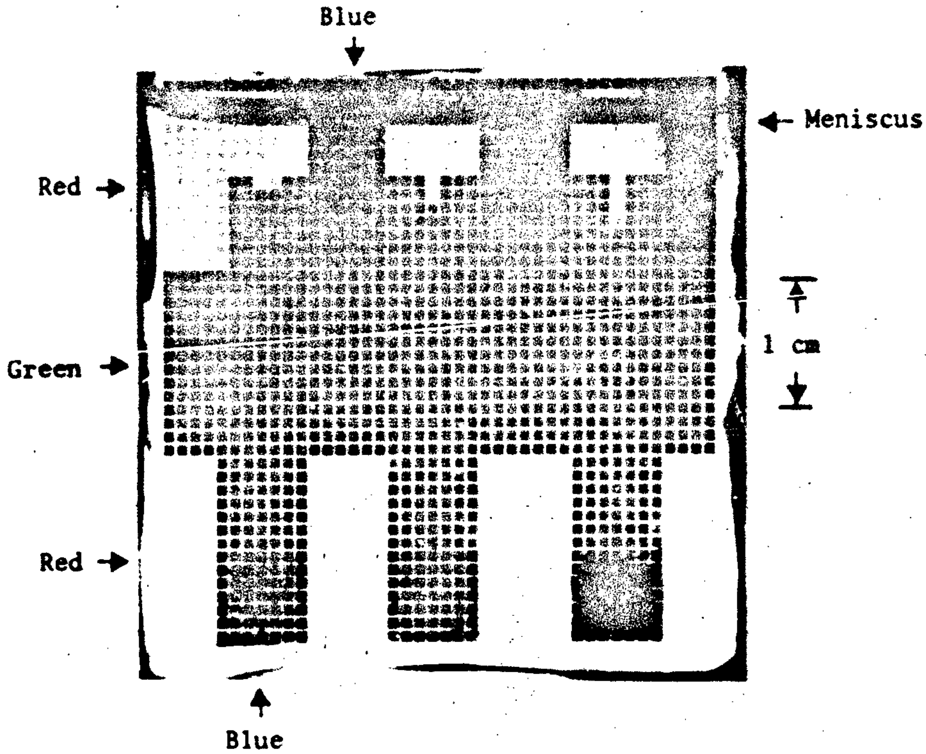
Figure 16. Dependence of Charge Density on Extrapolated Initial Current Density

C. RESOLUTION AND MEMORY

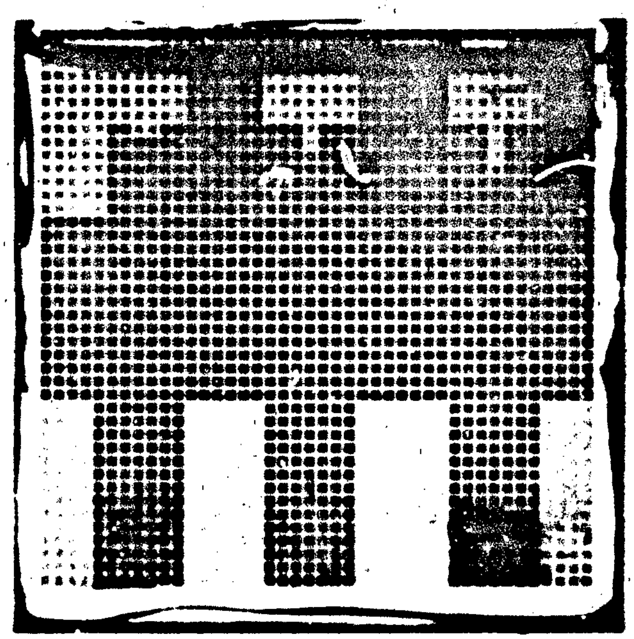
Each dot in a matrix display must be independently addressable. Its color must not be influenced by that of the surrounding region, even on standing. When these conditions are met, the display is said to have resolution and memory at the number of lines per inch characteristic of the plate design.

Lutetium diphthalocyanine responds to positive input voltages through the electrochemical oxidation reaction involving removal of electrons and injection of anions. This process changes the color from green to red. When a negative voltage is applied, the green dye undergoes a reduction process with injection of electrons and cations. It then turns blue-green, blue, or violet. Two dots that have been charged by opposite voltage pulses are capable of acting as a battery if they are connected by an electronic conductor while submerged in the electrolyte. A red dot and a blue dot interacting in this way will return spontaneously to green. For this reason, multiplexed addressing is not suitable. Even though thresholds exist in the responses of color to the driving voltage,[11] electronic isolation of the dots is essential to achieve memory. This requires complete etching of isolation lines in the transparent conductor. It also requires that the dye film be discontinuous in the line areas, since it too is electronically conductive while in the green state.

Test panels for the demonstration of resolution and memory at 24 lpi were fabricated by means of the masks shown in Figure 4. However, through a processing error, the insulated and bare tin oxide areas were inadvertently reversed This problem was discovered too late for correction within the contract period. Although the resulting pattern did not show one on two red dots surrounded by blue, or the inverse of this, as planned, it did produce large red and blue areas adjacent to one another. Figure 17 shows that those adjacent areas were switched



(a) Immediately After Switching



(b) After 10 min on Memory

Figure 17. Photographs of Resolution/Memory Panel

independently with good pattern definition. Only moderate fading of the image occurred in 10 min on open circuit. The fading probably was due more to incomplete etching of the plate than to direct chemical reactions of the dye. With heavily scribed lines in the tin oxide, other model cells have retained adjacent red and blue stripes at least 3 days.

IV. CONCLUSIONS

The lutetium diphthalocyanine system is capable of producing an attractive multicolor dot-matrix display with good legibility and memory at 24 lpi. Higher resolution should be attainable with essentially the same fabrication techniques. Integrated matrix drive circuitry will be needed to construct a fully operational matrix in which each dot is independently addressable.

The conclusions below are drawn from a brief transient study in which approximate circuit parameters were determined for the green-to-red switching process.

(1) A series resistance-capacitance model is useful in discussion of the display transients, even though the equivalent-circuit components are current- or voltage-dependent. The apparent capacitance C_o associated with the electrochromic process is essentially proportional to the electrode area, while the apparent resistance R_o is inversely proportional to area.

(2) For a relatively thick dye film with an inital optical density of 1.30, the capacitance term C_o/A is 800 to 1,500 $\mu f/cm^2$, depending on the height of the input voltage pulse, and the area resistance term R_oA is typically <25 $ohms \cdot cm^2$. Resistance effects of the electrolyte and the tin oxide were negligible with the cell arrangement used for the transient measurements.

(3) A time constant τ_o of 10 to 20 ms is characteristic in switching this film from green to red.

(4) The parameters R_oA, C_o/A, and τ_o are inherent in the electrochromic process at the dye thickness used.

(5) If the power were applied to a dot matrix through a large transparent drive plate, the substrate resistance effect could still be negligible, even at high resolution. This was shown by a simple mathematical model. The resistance of the individual switch, or driver, must also be low in comparison with R_o for the dot. For example, at 24 lpi, the driver resistance should be <<3000 ohms.

Further work toward the development of phthalocyanine dot-matrix displays is merited on the basis of this feasibility study.

V. RECOMMENDATIONS FOR FURTHER WORK

The following tasks are recommended for further development of multicolor electrochromic matrix displays based on the diphthalocyanines:

(1) Improvement of color contrast and cycle life through experimentation designed for these objectives. This work should be done with simple laboratory cells rather than complete matrix panels.

(2) Evaluation of other compounds in the dipthalocyanine series.

(3) Adaptation of integrated matrix drive to the diphthalocyanine electrochromic system.

VI. ACKNOWLEDGMENTS

Acknowledgments are due to P. E. Green for development of the computer-aided mask-design data and to A. M. Clark for experimental assistance in fabrication of the display plates. R. V. Galiardi contributed to early phases of the design work.

VII. GLOSSARY OF SYMBOLS

A	Electrode area
C	Capacitance
C_o	Effective capacitance of dye electrode without added resistance
E_1	Open-circuit potential of dye electrode in green state
E_2	Pulse potential for switching from green to red
E_3	Pulse potential for switching from red to green
E_4	Final potential, 10 mV more positive than E_1
	(All potentials are given vs Ag/AgCl reference electrode.)
E'	Back emf due to the electrochromic system
i	Current
$i_{t=o}$	Extrapolated current at $t = o$
n	Number of electrons transferred per molecule of dye in the electrochromic reaction
q	Charge for green-to-red switching
q_{lim}	Charge at maximum in trace of q vs t
R	Resistance
R_a	Added resistance in series with display electrode
R_c	Resistance of transparent conductor
R_o	Effective resistance of display electrode system
R_t	Total resistance in display electrode circuit
r	Radial distance in mathematical model of display substrate
r_o	Radial distance to metal contact in mathematical model
r_i	Radius of circular dye dot in mathematical model
t	Time
ρ_s	Sheet resistivity of transparent conductor
τ	Time constant of electrochromic process based on simple resistance-capacitance model
τ_o	Time constant without added series resistance

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